this end, we have studied the mechanism of reactions of $Cp_2V_2(CO)_5$ with donor ligands and we describe these in a separate publication.[26]

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Registry No. Ia, 41699-43-8; Ib, 12185-41-0.

Supplementary Material Available: Listings of observed and calculated structure factors and anisotropic thermal parameters for $Cp_2V_2(CO)_4PPh_3$ and $Cp_2V_2(CO)_5$ and also positional parameters for $Cp_2V_2(CO)_5$ (80 pages). Ordering information is given on any current masthead page.

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[26] Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 1840.

Contribution from the Department of Chemistry and Molecular Structure Center,
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Hexaisopropoxybis(dimethylamino)dinitrosyldimolybdenum

MALCOLM H. CHISHOLM,* JOHN C. HUFFMAN, and RAYMOND L. KELLY

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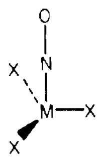
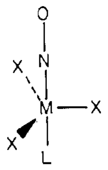
Hydrocarbon solutions of $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$ react with dimethylamine to form $Mo_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2(NO)_2$ as a fine microcrystalline precipitate. $Mo_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2(NO)_2$ shows little solution chemistry: it is only very sparingly soluble in hydrocarbon solvents, and in those which it does dissolve it exists in equilibrium with $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$ and free dimethylamine. The compound is also thermally unstable, readily eliminating the coordinated amine with the formation of $Mo_2(O\text{-i-}Pr)_6(NO)_2$. The molecular structure has a center of symmetry. Each molybdenum atom is in a distorted octahedral environment, and the halves of the molecule are joined through the agency of a pair of isopropoxy bridges; the Mo-to-Mo distance is 3.390 (2) Å, consistent with the absence of a metal-to-metal bond. There is a linear Mo–N–O moiety (179.4 (5)°) with a short Mo–N distance (1.763 (6) Å). In the infrared spectrum a band at 1617 cm^{-1} is assignable to $\nu(NO)$. These results are compared with other recently characterized alkoxynitrosyl compounds of the group 6 transition elements. Crystal data and cell dimensions for $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2(HNMe_2)_2$ are as follows: space group $P2_1/c$, $a = 9.889$ (2) Å, $b = 11.107$ (2) Å, $c = 16.901$ (3) Å, $V = 1576.9$ Å^3, $\beta = 121.85$ (2)°, $Z = 2$.

Introduction

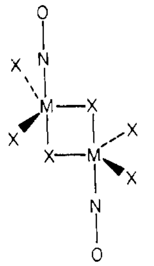
Prior work[1-3] has established that the group 6 transition elements form a related series of trialkoxynitrosyl complexes which may take the form of I, II, or III.



I



II

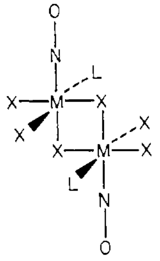


III

In I, II, and III there are linear M–N–O groups and the local geometry about the metal atoms contains a trigonal group of alkoxy ligands. Thus when the M–N–O molecular axis is defined as the z axis, there are four electrons in d_{xz} and d_{yz} metal atomic orbitals which are not appreciably used in metal–ligand σ bonding but which are extensively used in metal-to-nitrosyl π^* back-bonding. We report here the preparation and structural characterization of a fourth type of complex in which the metal atom is in a six-coordinate environment as shown in IV.

Results

Synthesis and Physicochemical Properties of $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2(HNMe_2)_2$. Hydrocarbon solutions of $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$ react with $HNMe_2$ to yield $Mo_2(O\text{-i-}Pr)_6(NO)_2(HNMe_2)_4$ as a microcrystalline red precipitate. The compound is sensitive to moisture and oxygen and must be handled in dry and oxygen-free atmospheres and solvents.



IV

$Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2(HNMe_2)_2$ is thermally unstable: when it is heated in vacuo, dimethylamine is given off and only $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$ can be sublimed. In the mass spectrometer the ion of highest mass corresponded to $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2^+$.

$Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2(HNMe_2)_2$ is only sparingly soluble in hydrocarbon solvents, and ^1H NMR spectra obtained in toluene-d_8 indicate that when it dissolves, it goes into solution to form an equilibrium mixture of $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2(HNMe_2)_2$, $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$, and dimethylamine. ^1H NMR spectra recorded in the presence of excess dimethylamine are consistent with the view that $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2(HNMe_2)_2$ maintains in solution the structure found in the solid state. Specifically there are three overlapping septets of equal integral intensity in the methyne proton region of the spectrum, as expected for the structure shown in Figure 1 which has three pairs of symmetry related O-*i*-Pr groups. The methyl groups of each of these O-*i*-Pr ligands are diastereotopic, and thus six doublets are expected in the isopropoxy methyl region of the spectrum. However, even at 220 MHz we have been unable to separate these: the spectrum simply reveals several overlapping doublets.

Infrared and ^1H NMR data are recorded in the Experimental Section.

Solid-State Structure. In the crystalline state the compound is composed of discrete molecules of $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$-

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(1) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 3354.
(2) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *Inorg. Chem.* **1979**, *18*, 116.
(3) Bradley, D. C.; Newing, C. W.; Chisholm, M. H.; Haitko, D. A.; Kelly, R. L.; Little D. A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.*, in press.
(4) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Reichert, W. W. *Inorg. Chem.* **1978**, *17*, 2944.

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Table I. Fractional Coordinates for $Mo_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2(NO)_2$[a]

atom	10^4x	10^4y	10^4z	$10B_{iso}$, $Å^2$
Mo(1)	3345.9 (5)	244.7 (4)	−1062.3 (3)	15
O(2)	5911 (6)	−133 (4)	−326 (3)	16
O(3)	−151 (4)	661 (5)	−1961 (3)	29
O(4)	3957 (4)	1917 (4)	−978 (2)	17
O(5)	3236 (6)	−160 (4)	−2191 (3)	20
N(6)	3119 (5)	−1802 (5)	−929 (3)	20
N(7)	1284 (8)	496 (5)	−1590 (4)	21
C(8)	3021 (8)	2938 (6)	−1470 (5)	28
C(9)	2600 (28)	3670 (12)	−945 (10)	118
C(10)	3861 (22)	3690 (13)	−1785 (14)	121
C(11)	1995 (9)	−17 (7)	−3136 (5)	24
C(12)	1619 (11)	8785 (9)	6370 (7)	57
C(13)	2566 (17)	875 (13)	−3580 (7)	82
C(14)	6713 (8)	−262 (5)	−840 (5)	22
C(15)	8176 (8)	−990 (6)	−344 (5)	31
C(16)	6974 (7)	944 (6)	−1134 (4)	27
C(17)	1520 (7)	7746 (7)	8765 (5)	36
C(18)	3846 (9)	−2594 (6)	−1300 (5)	32
H(19)	3490	−1936	−400	30
H(20)	2145	2602	−2011	30
H(21)	3409	3876	−174	30
H(22)	1938	4405	−1346	30
H(23)	1743	3168	−898	30
H(24)	4426	3456	−1866	30
H(25)	3438	4362	−2112	30
H(26)	4614	4233	−1221	30
H(27)	961	319	−3128	30
H(28)	648	−1118	−4313	30
H(29)	2680	−1545	−3537	30
H(30)	1489	−1818	−3316	30
H(31)	3755	750	−3322	30
H(32)	2390	1666	−3428	30
H(33)	1952	774	−4226	30
H(34)	5865	−741	−1378	30
H(35)	8547	−1108	−735	30
H(36)	8283	−1690	−47	30
H(37)	9030	−547	214	30
H(38)	5871	1357	−1545	30
H(39)	7271	867	−1598	30
H(40)	7594	1306	−616	30
H(41)	1023	−1788	−960	30
H(42)	693	−2212	−1913	30
H(43)	1402	−3106	−1041	30
H(44)	3101	−2593	−1994	30
H(45)	3985	−3397	−1058	30
H(46)	4879	−2308	−1130	30

[a] The isotropic thermal parameters listed for those atoms refined anisotropically are the isotropic equivalents. Numbers in parentheses in this and all following tables refer to the error in the least significant digits.

Table II. Bond Distances in Angstroms for $Mo_2(O\text{-}i\text{-}Pr)_6(HNMe_2)(NO)_2$

A	B	dist
Mo(1)	Mo(1)′	3.390 (2)
Mo(1)	O(2)′	2.062 (5)
Mo(1)	O(2)	2.196 (5)
Mo(1)	O(4)	1.935 (4)
Mo(1)	O(5)	1.909 (5)
Mo(1)	N(6)	2.306 (5)
Mo(1)	N(7)	1.763 (6)
O(2)	C(14)	1.461 (9)
O(3)	N(7)	1.224 (8)
O(4)	C(8)	1.421 (8)
O(5)	C(11)	1.419 (9)
N(6)	C(17)	1.468 (8)
N(6)	C(18)	1.470 (10)
C(8)	C(9)	1.419 (14)
C(8)	C(10)	1.465 (16)
C(11)	C(12)	1.510 (12)
C(11)	C(13)	1.521 (17)
C(14)	C(15)	1.472 (10)
C(14)	C(16)	1.499 (10)

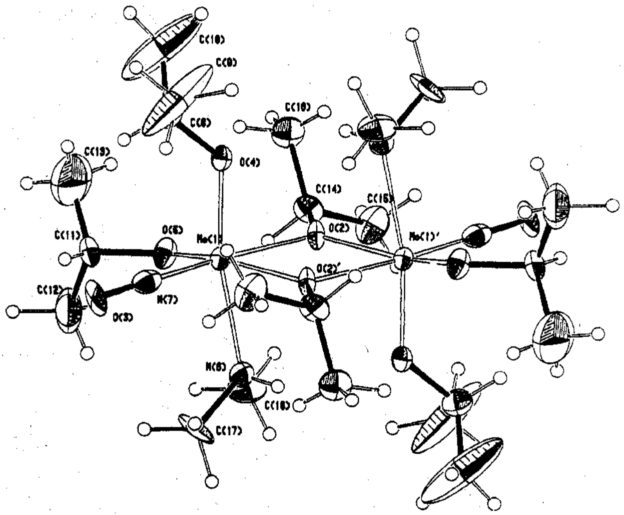

Figure 1. ORTEP drawing of the $Mo_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2(NO)_2$ molecule showing the atomic-numbering scheme used in the tables. Thermal ellipsoids are drawn at the 50% probability level.

Table III. Bond Angles in Degrees for $Mo_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2(NO)_2$

A	B	C	angle
O(2)′	Mo(1)	O(2)	74.5 (2)
O(2)′	Mo(1)	O(4)	93.7 (2)
O(2)	Mo(1)	O(4)	85.4 (2)
O(2)	Mo(1)	O(5)	87.7 (2)
O(2)′	Mo(1)	O(5)	157.5 (2)
O(2)′	Mo(1)	N(6)	79.9 (2)
O(2)	Mo(1)	N(6)	84.2 (2)
O(2)	Mo(1)	N(7)	176.0 (2)
O(2)′	Mo(1)	N(7)	101.9 (2)
O(4)	Mo(1)	O(5)	98.7 (2)
O(4)	Mo(1)	N(6)	168.9 (2)
O(4)	Mo(1)	N(7)	96.7 (2)
O(5)	Mo(1)	N(6)	84.7 (2)
O(5)	Mo(1)	N(7)	95.3 (2)
N(6)	Mo(1)	N(7)	93.4 (2)
Mo(1)	O(2)	Mo(1)′	105.5 (2)
Mo(1)	O(2)	C(14)	120.6 (4)
Mo(1)	O(2)	C(14)	134.0 (4)
Mo(1)	O(4)	C(8)	129.9 (3)
Mo(1)	O(5)	C(11)	131.2 (4)
Mo(1)	N(6)	C(17)	116.4 (4)
Mo(1)	N(6)	C(18)	117.0 (4)
C(17)	N(6)	C(18)	108.8 (5)
Mo(1)	N(7)	O(3)	179.4 (5)
O(4)	C(8)	C(9)	114.0 (6)
O(4)	C(8)	C(10)	110.4 (7)
C(9)	C(8)	C(10)	108.2 (10)
O(5)	C(11)	C(12)	109.8 (6)
O(5)	C(11)	C(13)	107.7 (6)
C(12)	C(11)	C(13)	110.3 (9)
O(2)	C(14)	C(15)	113.2 (6)
O(2)	C(14)	C(16)	110.7 (5)
C(15)	C(14)	C(16)	113.0 (6)

$(HNMe_2)_2$. An ORTEP view of the molecule indicating the coordination geometry and the atom-numbering scheme is shown in Figure 1. Final atomic coordinates and isotropic[5] thermal parameters are given in Table I. Complete listings of bond distances and angles are given in Tables II and III, respectively.

The molecule has a center of inversion which relates in a pairwise manner the halves of the dimer. The local geometry about each molybdenum atom is that of a distorted octahedron;

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(5) Anisotropic thermal parameters are given in the supplementary data. The complete structural report of the supplementary material, MSC Report 7915, is available upon request in microfiche form only from the Indiana University Chemistry Library.

there are three pairs of O-*i*-Pr ligands (a bridging pair, a pair trans to $HNMe_2$ ligands, and a pair trans to bridging O-*i*-Pr ligands) and four distinct Mo–O bond distances. The Mo–O distances associated with the bridging O-*i*-Pr groups are significantly longer than those associated with terminal O-*i*-Pr ligands. Also significant is the observation that the Mo–O distance (2.196 (5) Å) trans to the nitrosyl ligand is longer than the Mo–O distance (2.062 (5) Å) of the bridging O-*i*-Pr ligand which is trans to a terminal O-*i*-Pr ligand. This observation indicates that, within the same molecule, a linear M–NO group exerts a higher trans influence than a terminal OR ligand. This conclusion was inferred previously from a comparison of the structures of the $Mo_2(O\text{-}i\text{-}Pr)_8$ and $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$ molecules.[4]

The Mo-to-Mo distance is 3.390 (2) Å which is comparable to that found in $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$ (3.335 (2) Å). The short No–N(nitrosyl) and long N–O distances are also comparable to those found in $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$. The Mo–N distance of the coordinated dimethylamine molecule is very long 2.306 (5) Å, longer than that found in *trans*-$Mo(OSiMe_3)_4(HNMe_2)_2$ (2.219 (4) Å) which is consistent with the view that it is relatively weakly bound.

Discussion

This work shows that molybdenum in $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$ is capable of expanding its coordination number from five to six and the reversible addition of dimethylamine interconverts compounds of general formula III and IV. The addition of dimethylamine to $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$ yields $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2(HNMe_2)_2$ by the formation of relatively weak Mo–N bonds in cis positions to the nitrosyl ligand. In this regard it is interesting to note that the addition of a fourth σ donor ligand to what was formerly the trigonal plane of equatorial O-*i*-Pr ligands in $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$ has a relatively small effect on metal d to nitrosyl π^* back-bonding as evidenced by ν(NO) values. Compare $\nu(NO) = 1632\ cm^{-1}$ in $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$ with $\nu(NO) = 1617\ cm^{-1}$ in $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2(HNMe_2)_2$. This observation is consistent with the view that the energies of the metal d orbitals used in π bonding to the nitrosyl ligand are not greatly influenced by the σ-bonding skeleton of the molecule but are very sensitive to π-donor properties of the ligands.[3] It is possible and quite likely that compounds of type I and IV are intermediates in reactions interconverting compounds II and III. I and IV are intermediates of limiting S_N1 and S_N2 processes. In the study of the reaction between $Cr_2(O\text{-}i\text{-}Pr)_6(NO)_2$ and 2,4-lutidine which gives $Cr(O\text{-}i\text{-}Pr)_3(NO)(L)$, we present evidence supporting the view that chromium reacts via an initial bond dissociation.[3] That molybdenum in $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$ is capable of reacting via ligand association with dimethylamine probably reflects the relative size of the two metals, Mo > Cr.

$$\underset{\text{III}}{M_2(OR)_6(NO)_2} + 2L \rightleftharpoons \underset{\text{II}}{2M(OR)_3(NO)L}$$

Experimental Section

General procedures and the preparation of $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$ have been described previously.[1]

Preparation of $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2(HNMe_2)_2$. To $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$ (0.194 g, 0.32 mmol) in toluene (5 mL) was added $HNMe_2$ (0.64 mmol) by use of a calibrated vacuum manifold. Upon the addition of $HNMe_2$ the color of the solution changed from yellow to red. The solution was stirred for ca. 2 h during which time a microcrystalline red precipitate formed. The precipitate was collected by filtration and dried in vacuo, yielding $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2(HNMe_2)_2$ (ca. 200 mg). Anal. Calcd: C, 37.7; H, 8.06; N, 8.00. Found: C, 37.4; H, 7.94; N, 7.93. IR data obtained from a Nujol mull between NaCl plates: 3175 (w, br), 1617 (s, br), 1324 (m), 1210 (w), 1164 (m), 1112 (s), 1022 (w), 964 (s, br), 938 (m), 927 (w), 905 (w), 840 (m), 818 (w), 720 (w), 644 (m). ^1H NMR data obtained in toluene-d_8 at 16 °C, 220 MHz in the presence of excess $HNMe_2$: δ(CH) 5.44, 5.29, 5.44 (relative to Me_4Si); overlapping septets of equal intensity.

X-ray Structural Determination. A crystal of maximum dimension 0.44 mm was mounted in a nitrogen-filled glovebag and transferred to the liquid-nitrogen boil-off cooling system of the diffractometer.[6] The diffractometer used for data collection was designed and constructed locally. A Picker four-circle goniostat equipped with a Furnas monochromator highly oriented graphite crystal, 002 plane, and Picker X-ray generator is interfaced to a TI 980 minicomputer, with Slo-Syn stepping motors to drive the angles. Centering is accomplished by using automated top/bottom–left/right slit assemblies. The minicomputer is interfaced by low-speed data lines to a CYBER 172-CDC 6600 multimainframe system where all computations are performed.

The cell dimensions and crystal data obtained from 20 reflections at −145 °C by using Mo Kα', $\lambda = 0.71069$ Å, were $a = 9.889$ (2) Å, $b = 11.107$ (2) Å, $c = 16.901$ (3) Å, $\beta = 121.85$ (2)°, $V = 1576.89$ Å^3, $Z = 2$, $d_{calcd} = 1.466\ g\ cm^{-3}$, and space group $P2_1/c$.

A total of 2705 reflections were collected by using standard moving-crystal–moving-detector techniques with the following values: scan speed = 3° min^{-1}; scan width = 2 + dispersion; single background time at extremes of scan = 10 s; aperture size = 2.5 × 3.5 mm. Data were corrected for absorption on the basis of crystal dimensions of [0,1,1] = 0.18 mm, [0,−1,−1] = 0.18 mm, [−1, 0,2] = 0.22 mm, [0,1,−1] = 0.22 mm, [1,1,−1] = 0.21 mm, [1,$\bar{1}$,1] = 0.21 mm, and [1,1,2] = 0.13 mm. After reduction in the usual manner, 2705 unique intensities were obtained. The number of reflections with $F > 2.33\ \sigma(F)$ was 2025.

The structure was solved by using the direct methods (LSAM) programs in the XTEL library, and the Mo position was confirmed by using Patterson techniques. Since the crystal was well-defined, an absorption correction was applied (minimum and maximum were 0.684 and 0.790, respectively). The nonhydrogen atoms refined normally although several atoms had large thermal parameters. All hydrogens were located in subsequent difference Fourier synthesis phased on the nonhydrogen data. Attempts to refine the hydrogen atoms failed, as several would not converge, even while thermal parameters were held fixed. For this reason hydrogens were refined by using Fourier techniques (i.e., the hydrogens were relocated after each cycle of refinement and placed in fixed positions with $B_{iso} = 3.0$ Å^2 for subsequent cycles). The hydrogens are thus not considered well located, although all positions and geometrical parameters are consistent with what one would expect.

The final residuals based on all nonzero data were $R(F) = 0.055$ and $R_w(F) = 0.121$. The goodness-of-fit for the last cycle was 2.66 and the maximum Δ/σ was 0.19. The large value of the goodness-of-fit indicates that the "ignorance factor" used in data reduction ($\rho = 0.05$) was underestimated. The rather large value of $R_w(F)$ reflects the subsequent error in weighting.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, the Marshal H. Wrubel Computing Center, and the taxpayers of the State of Indiana for financial support of this work. We thank Professor D. C. Bradley and Mr. Peter Cook, Queen Mary College, London University, for obtaining mass spectral data.

Registry No. $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2(HNMe_2)_2$, 74063-04-0; $Mo_2(O\text{-}i\text{-}Pr)_6(NO)_2$, 67414-89-5.

Supplementary Material Available: Tables of anisotropic thermal parameters and observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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[6] Huffman, J. C. Ph.D. Thesis, Indiana University, Bloomington, IN, 1974.